2018 DOE Vehicle Technologies Office Annual Merit Review Poster Presentation

Li-Ion Battery Anodes from Electrospun Nanoparticle/Conducting Polymer Nanofibers

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June 19, 2018

Project ID bat264

Overview

Timeline

- October 1, 2015
- September 30, 2019
- Percent complete: 60%

Budget

- Total project funding
  - DOE $590,000
  - Contractor $117,062 (VU)
- Funding for FY 2017: $180,000
- Funding for FY 2018: $230,000

Barriers

- Barriers addressed
  - Capacity fade when using Si as the anode material in a Li-ion battery
  - Achieving high volumetric, gravimetric, and areal energy densities at moderate C-rates
- Targets
  - Gravimetric capacity: 1,200 mAh/g (0.1C)
  - Areal capacity: 3 mAh/cm^2 (0.1C)
  - Volumetric capacity: 800 mAh/cm^3 (0.1C)
  - 40% capacity retention at 2C

Partners

- Lawrence Berkeley National Lab
- Oak Ridge National Lab
- e-Spin Technologies, Inc.
- **Project Lead: Peter N. Pintauro, Vanderbilt**

Project Relevance and Objectives

Project Objective:

To fabricate and characterize nanofiber anode mats containing Si nanoparticles and an electronically conductive particles or conductive polymer binder for Li-ion batteries, where the mats exhibit:
- High gravimetric, areal, and volumetric capacities
- Long cycle life (90% capacity retention after 200 cycles at 0.1C)
- Good performance at high C-rates (e.g., 500 mAh/g at 2C)

Relevance:

Address problems with conventional thin film Si slurry anodes: (**i**) Low area capacity (the need to use only thin electrodes), (**ii**) Poor volumetric and/or areal energy densities at high C-rates, (**iii**) Si expansion/contraction result in electrode deterioration during cycling.

2017-2018 Project Tasks/Goals:

1. Fabricate and investigate/evaluate dual-fiber Si/PAA-C/PAN anodes.
2. Test cycling stability of the new anodes in half cells.
3. Assemble Si/PAA-C/PAN anode and NMC cathode in a full cell and test its cycling stability.

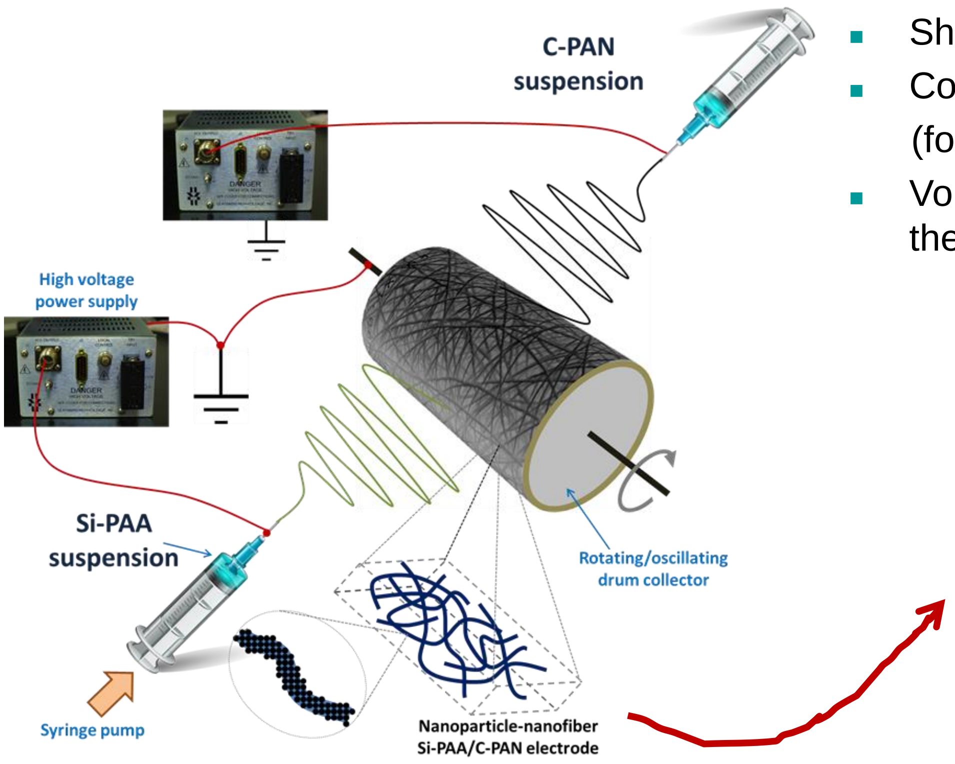
Milestones

Month/Year	Milestone or Go/No-Go Decision	Status
September 2016	Go/No-Go Decision: Demonstrate an initial capacity above 500 mAh/g and 90% capacity retention after 50 cycles at 0.1C rate.	Complete
December 2016	Milestone: Demonstrate that at least one new conductive binder has been synthesized and is ready in sufficient quantity for electrospinning	Complete
March 2017	Milestone: Demonstrate at least one successfully electrospun composite anode containing at least 65% Si and/or SiO particles	Complete
June 2017	Milestone: Identify key structure/performance correlations for electrospun anodes	Complete
June 2018	Milestone: Electrospin different dual fiber mat anodes by changing binder type, Si/binder and carbon/binder wt. ratio of each fiber, and the wt. ratio of the two fiber types in an anode mat. Evaluate anodes in coin cells (half- and full cells at 1.0 and 2.0 mAh/cm^2) at 0.1 C and 1C.	On track
September 2018	Go/No-Go Decision: Demonstrate a discharge capacity of at least 750 mAh/g, after 50 cycles at 0.1C and a capacity above 500 mAh/g after 50 cycles at 1C, with an areal capacity of between 1.0 and 2.0 mAh/cm^2	On track
March 2019	Milestone: Identify the final anode composition/morphology and the final performance metrics	On track
June 2019	Milestone: Demonstrate performance data for anodes electrospun at commercial facility	On track
September 2019	Milestone: Demonstrate that the performance of scaled-up anodes matches/exceeds that from laboratory-fabricated anodes and meets the target performance metrics	On track

Approach

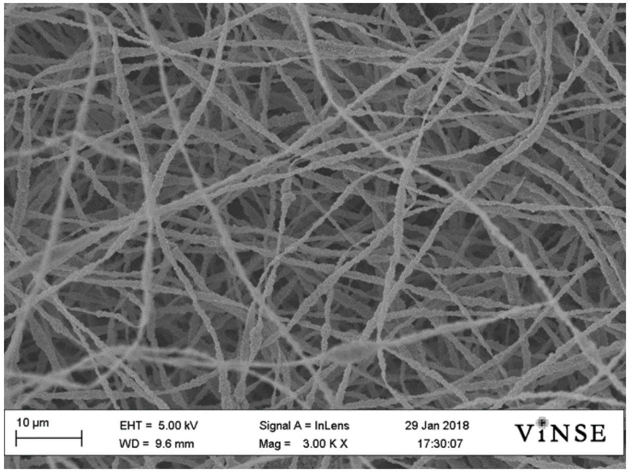
Dual Fiber Particle/Polymer Electrospinning

Electrospinning from two, separate spinnerets is used to obtain a porous, fibrous electrode composed of intermixed Si/PAA and C/PAN fibers.



Advantages of a Dual Fiber Anode:

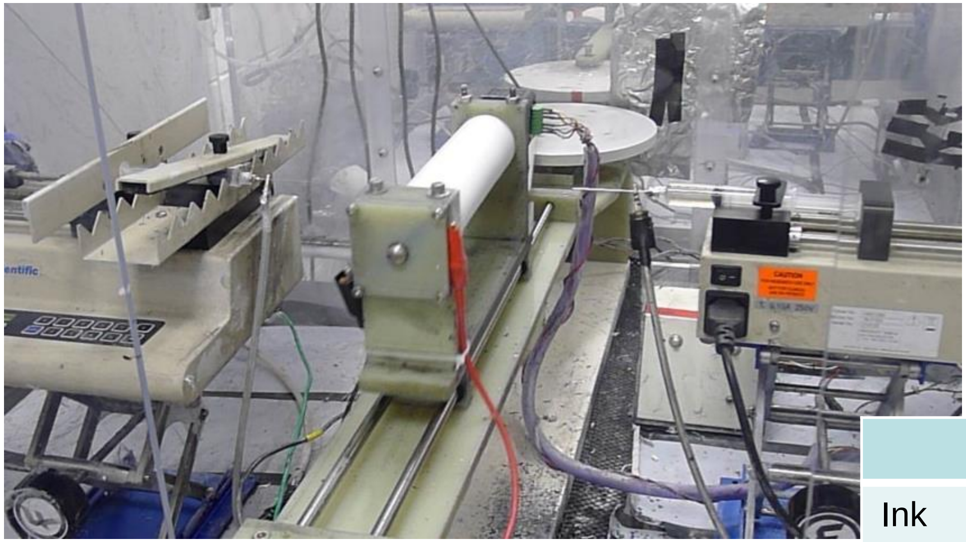
- High surface area/volume ratio
- Short Li^+ transport pathways
- Controllable fiber volume fraction
  (for high areal and volumetric capacity)
- Volume changes of Si/PAA network are stabilized by the interpenetrating C/PAN network, for long cycle life



SEM image of raw electrospun electrode (500 nm fibers)

Approach

Dual Fiber Particle/Polymer Electrospinning



Si-C-binder anodes were prepared by co-electrospinning Si-PAA fibers and C-PAN fibers onto a Cu foil.

	Si/PAA Fibers	C/PAN Fibers
Ink Composition	0.3 g Si (50-70 nm) 0.3 g PAA 2.0 g IPA 2.0 g MeOH	0.34 g C (Vulcan) 0.2 g PAN 2.75 g DMF
Bias Voltage	8.0 kV	9.0 kV
Spinneret-to-collector distance	7.5 cm	9.4 cm
Flow rate	0.85 ml/h	0.30 ml/h
Temp and humidity	24^{o}C and 30% RH	

Fiber mat was (i) compacted for 60 sec at 10 MPa and the welded (exposed to MeOH vapor for 30 minutes and DMF vapor for 30 minutes).

Mat was dried under vacuum (70^{o}C for 1 hour and then at 110^{o}C overnight).

<u>Example Final Mat Composition</u>:
70 wt% Si/PAA (50/50) fibers and 30% C/PAN (63.37) fibers. Si areal loading of 0.25 mg/cm^2.

Technical Accomplishments and Progress

Effect of PAN Content on Electrospun C-PAN Fiber Mats

The carbon fiber network in an anode plays two roles:

(1) Provides the necessary electronic conduction pathway, for transport of electrons to and from the Si-loaded fibers,

(2) Helps in maintaining the structural viability of the anode after repeated retraction of the expanded (charged state) Si fibers to their compact state, after the discharge.

It became important to determine the effect of PAN content on electrospinnability and on the resistance of the C-PAN processed mats

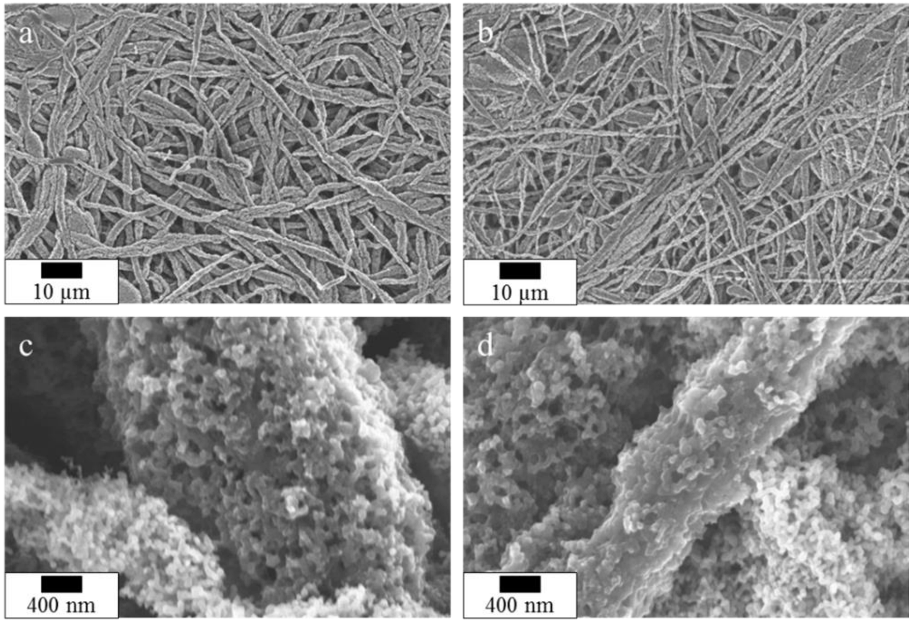
PAN Content (wt.%)	Area Specific Resistance ($\Omega \cdot cm^2$)	Electrospun Mat Quality
35	5.3	Poor
37	11.3	Medium
40	16.3	Good
42	21.5	Excellent

It appears, that PAN content at 37wt% is the optimum, giving both reasonably low resistance and acceptable mat quality/uniformity.

Technical Accomplishments and Progress

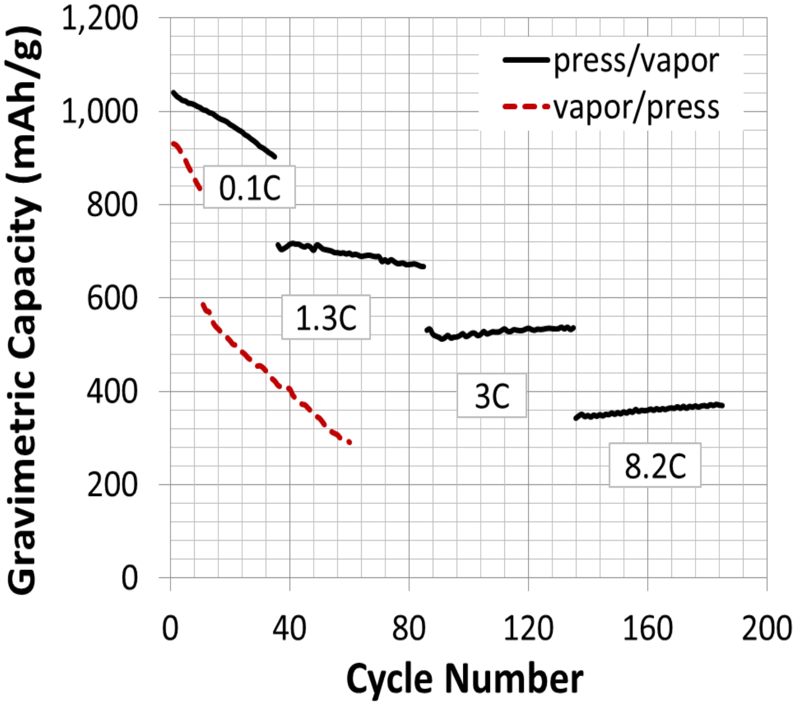
Dual Fiber Particle/Polymer Electrospinning

Press (to densify the electrode) and then solvent vapor exposure (to network the fibers) or solvent vapor exposure and then press**?**



Welded/Compacted

Compacted/Welded

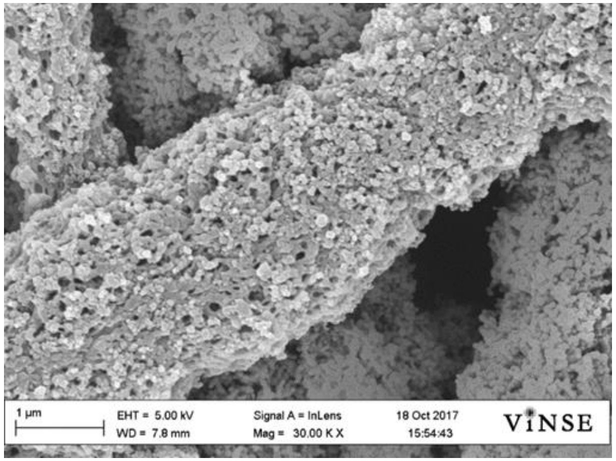


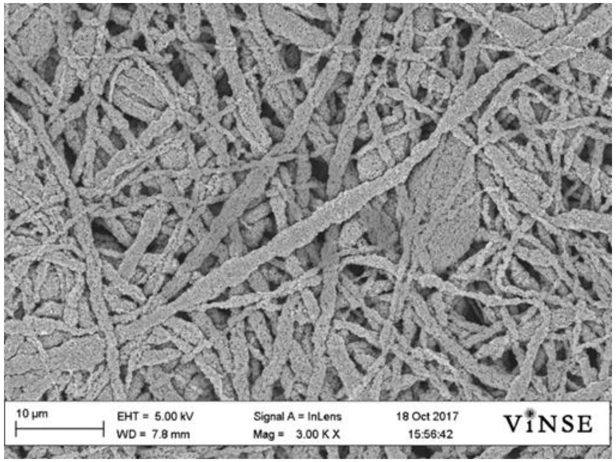
- Compaction and then vapor exposure (welding) is best.
- 93% capacity retention after 50 cycles at 1C.
- Half cell was tested for a total of 185 cycles.

- No obvious difference in dual fiber mat appearance
- <u>Pressing electrode before exposure to solvent vapor gives better result</u>

Technical Accomplishments and Progress

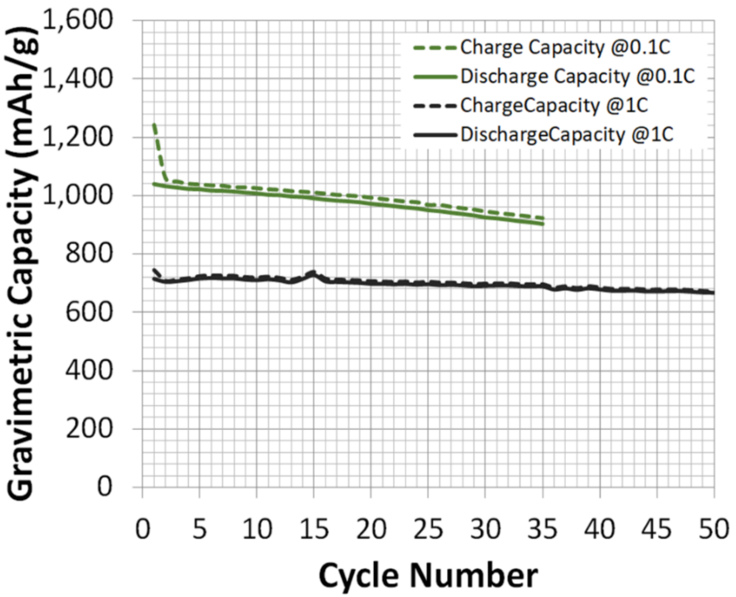
Dual Fiber Particle/Polymer Electrospinning





C/PAN fibers look much better than C/PAA fibers studied earlier. Now Si and carbon fibers are indistinguishable.

CR2032 half cell using a Li metal counter/reference electrode, Celgard 2500 separator, and an electrolyte containing 1.2 M $LiPF_6$ with 3/7 EC/DEC and 30% FEC additive



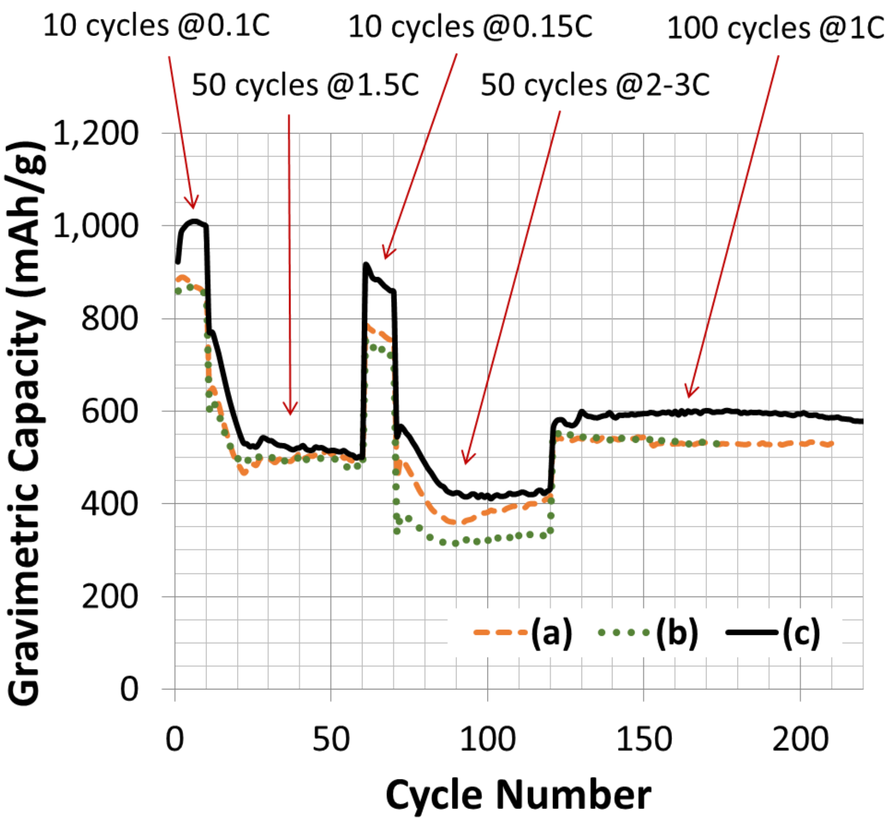
Capacity data collected at 0.1C for 35 cycles (87% capacity retention) and then at 1C for 50 cycles (94% capacity retention, cycle efficiency >98%).

Initial capacity per gram of Si is 3,543 mAh/g, based on the amount of Si electrospun; close to theoretical capacity of 3,600 mAh/g for $Li_{15}Si_4$. **We are getting complete utilization of the Si in a dual fiber anode**.

Areal capacity at 0.1C (after 35 cycles) is 0.64 mAh/cm^2.

Technical Accomplishments and Progress

Dual Fiber Particle/Polymer Electrospinning



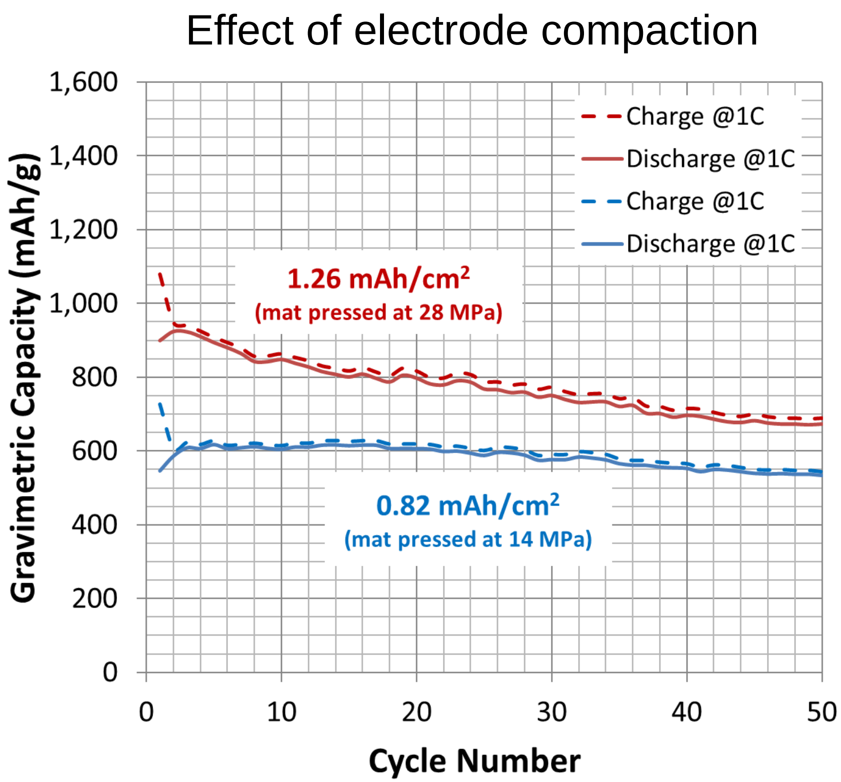
(a) 0.69 mg/cm^2
(b) 0.99 mg/cm^2
(c) 1.33 mg/cm^2

24 hour break (no load) before last 100 cycles at 1C

Anode (c) had a stable gravimetric capacity of 600 mAh/g at 1C (an areal capacity of 0.80 mAh/cm^2).

Technical Accomplishments and Progress

Dual Fiber Particle/Polymer Electrospinning



The dual fiber mat contained 35 wt.% Si nanoparticles, 25 wt.% C (Vulcan) and 40 wt.% binders (17 wt.% PAN and 23 wt.% PAA).

Red curves – electrode compacted at 28 MPa

Blue curves – electrode compacted at 14 MPa

- The red discharge curve meets one of the September 2018 targets: "capacity above 500 mAh/g after 50 cycles at 1C, with an areal capacity of between 1.0 and 2.0 mAh/cm^2".
- However, when the electrode is compacted less (blue curves), there is less capacity loss with cycle number.

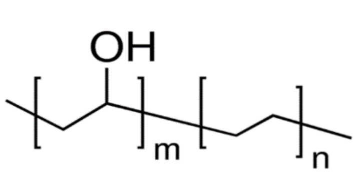
Technical Accomplishments and Progress

Electrospraying

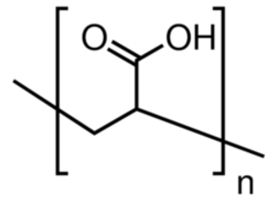
This simplified version of electrohydrodynamic processing does not require electrospinnable carrier/binder.

Binder is composed of poly(vinyl alcohol-co-ethylene) (PVAE)
+
Poly(acrylic acid) (PAA)

Thermal crosslinking (overnight at 110^{o}C) to generate esters



PVAE



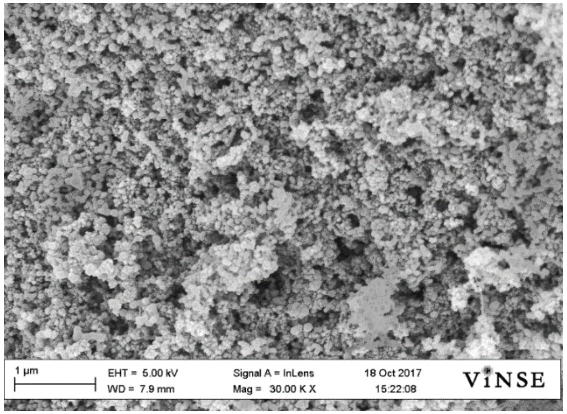
PAA

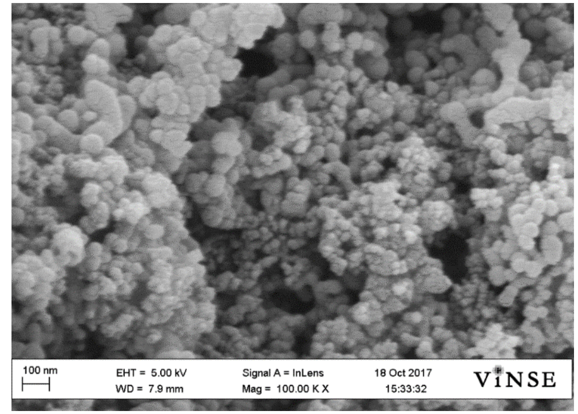
Ink Contained: 0.208 g Si, 0.13 g C, 0.091 G PVAE, and 0.091 g PA

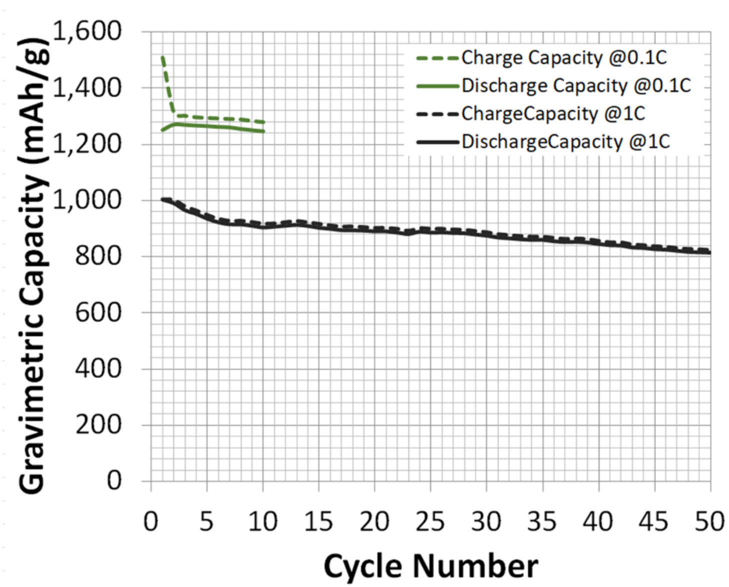
The ink could not be electrospun into fibers – there was only electrosprayed droplets. The droplet composition was 40/25/35 wt, ratio of Si/C/PVAE-PAA. The advantage of **this binder was that it could be thermally crosslinked**.

Technical Accomplishments and Progress

Electrospraying







Si areal loading was 0.15 mg/cm^2

Theoretical capacity, based on Si and C composition was 1515 mAh/g (close to what was seen after 1st discharge cycle).

At 1C, initial capacity was high (1,003 mAh/g)

After 50 cycles at 1C, capacity was 815 mAh/g (81% retention).

Coulombic efficiency during the last cycle was 98.9%.

Cycling stability somewhat lower compared to the dual fiber electrospun anode of the same areal capacity.

Technical Accomplishments and Progress

Electrospinning vs. Electrospraying

Dual Fiber Anode				Electrosprayed Anode		
C-rate	Discharge Capacity	Coulombic Efficiency		C-rate	Discharge Capacity	Coulombic Efficiency
0.14	903	97.8		0.10	1246	97.5
1.3	666	99.3		1.3	815	98.9
3.0	535	99.6		3.0	576	99.3
8.2	370	99.8		10.0	330	99.7

Data collected after 50 charge/discharge cycles for all C-rates except:
0.14 C-rate: dual fiber (collected after 35 cycles)
0.10 C-rate: electrosprayed (collected after 10 cycles).

All data were collected on one dual fiber and one electrosprayed coin cell.

Dual fiber areal loading: 0.80 mAh/cm^2 (after 50 cycles at 1.3C)
Electrosprayed anode: 0.35 mAh/cm^2 (after 50 cycles at 1.3 C)

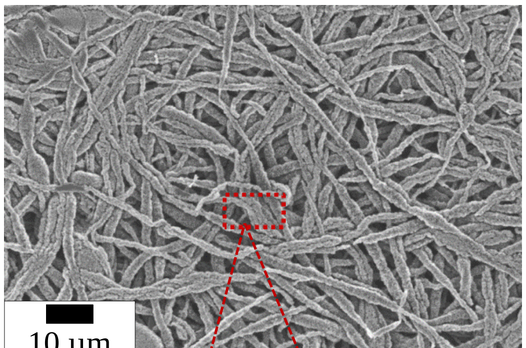
Higher initial gravimetric capacity at a given C-rate for the electrosprayed anode but its areal capacity was 2+ times lower.

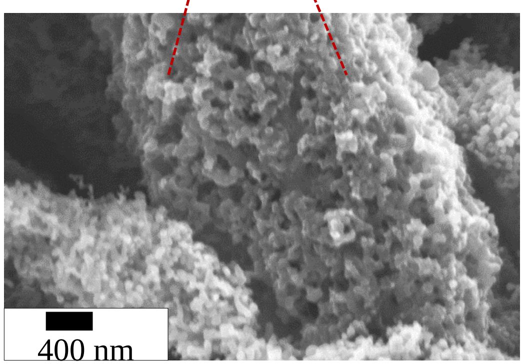
Technical Accomplishments and Progress

ORNL: Post-Mortem Electrode Characterization of dual fiber electrodes (ORNL)

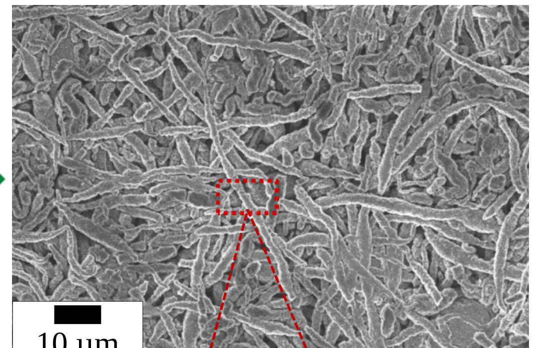
Goal: Determine how mat morphology changes upon cycling

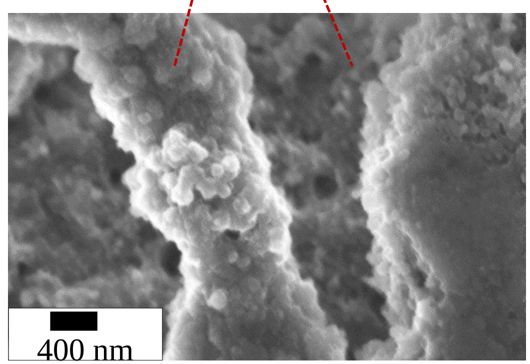
Pristine Mat





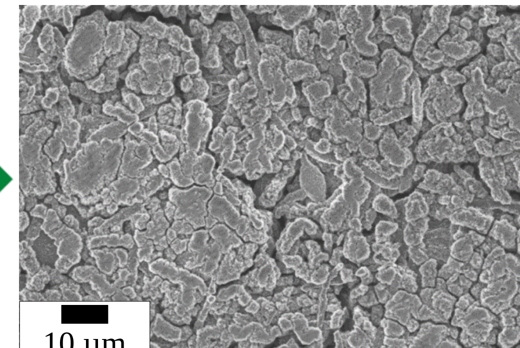
After 60 Cycles (0.1-1C)





SEI overgrowth on surface of individual fibers/particles

After 185 Cycles (0.1-8.2C)



SEI overgrowth throughout interfiber void space

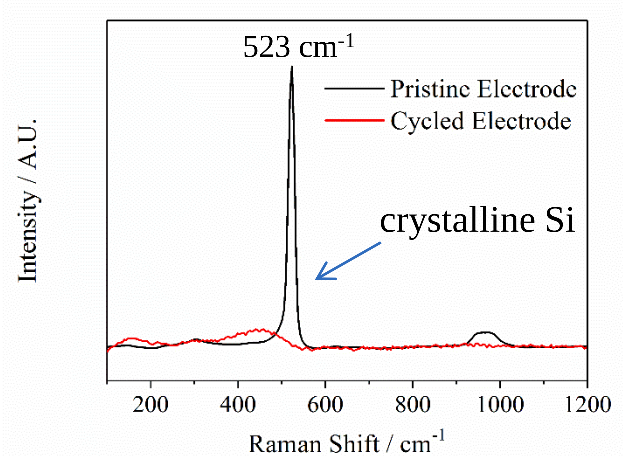
Longer cycling tests result in thick SEI layer which disrupts the electrode’s pore structure. Regardless, electrode exhibit a stable capacity of ~375 mAh/g at 8.2C after 185 cycles.

Technical Accomplishments and Progress

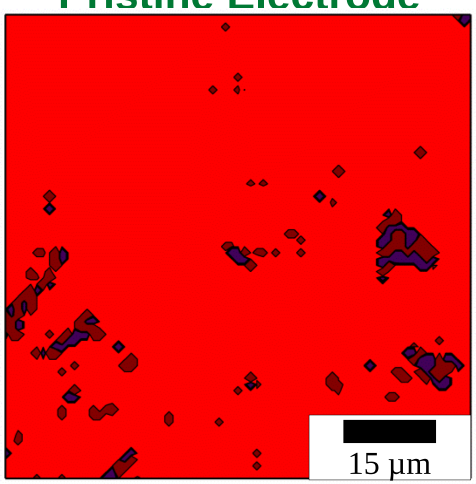
Cycling-Induced Structural Changes of Si (ORNL)

<u>Goal:</u> Understand how Si structure changes during electrochemical cycling

Raman Spectroscopy Mapping

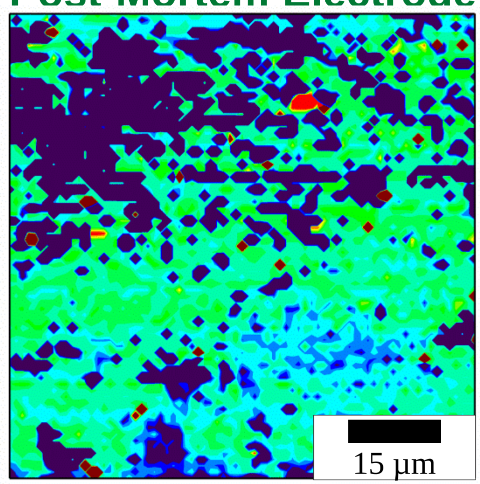


Pristine Electrode

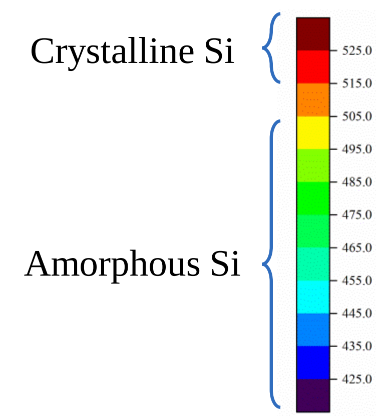


185 Cycles

Post-Mortem Electrode



Position of Maximum Peak (cm^{-1})



Raman spectroscopy shows that Si undergoes a crystalline to amorphous transformation during cycling. Virtually no crystalline Si was detected in the cycled electrode, indicating the **dual fiber electrode had sufficient electrical conductivity to promote complete active material utilization**. This conclusion is consistent with electrochemical experiments at VU.

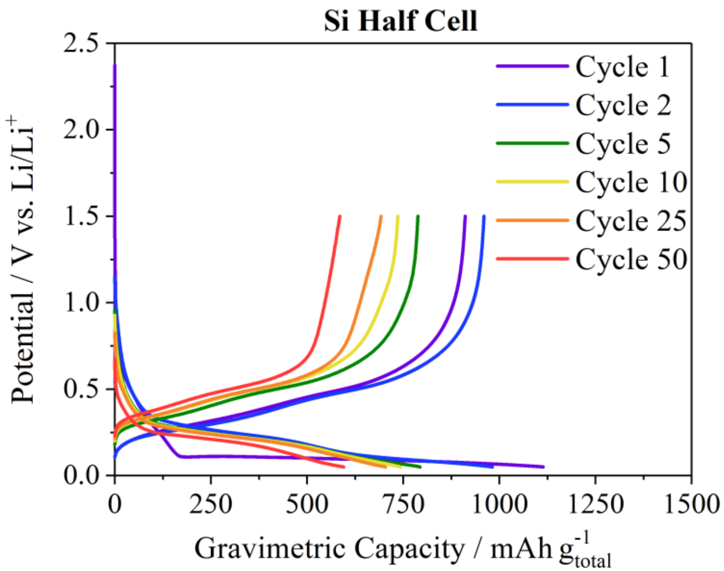
Technical Accomplishments and Progress

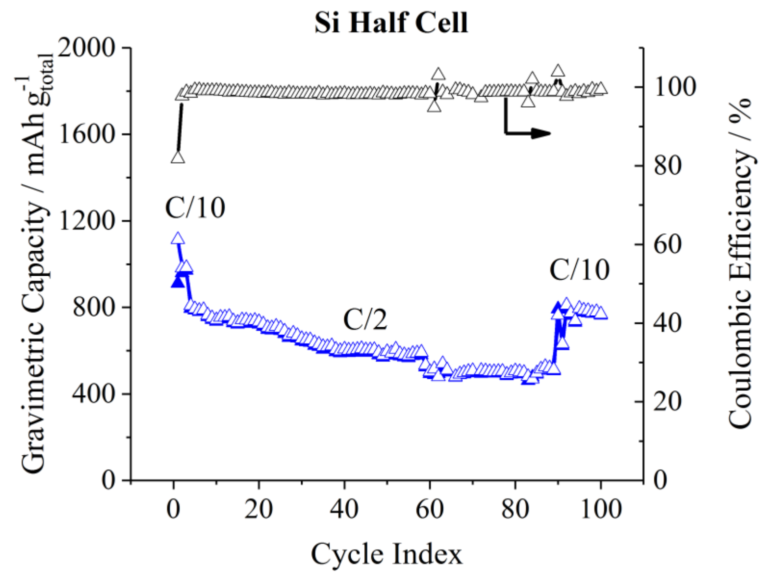
Dual Fiber Anodes – Half Cell Studies (ORNL)

Anode Composition (DF 112917)
26.1 wt% Si nanoparticles
21.8 wt% Conductive Carbon
52.1 wt% Binder

Electrochemical Cycling Procedure
Li metal counter/reference electrode
Galvanostatic charge/discharge, 0.05 – 1.5 V
C/10 (3 cycles), C/2 (86 cycles), C/10 (11 cycles)

Electrolyte Composition
Gen 2 Electrolyte (1.2 M $LiPF_6$ in 3/7 EC/EMC)
+ 10 wt% FEC Additive





- Dual fiber anode showed a high initial reversible capacity of 911 mAh/g_{total} (3,200 mAh/g_{Si}).
- Half cell showed moderate cycling stability (79% capacity retention after 100 cycles). This somewhat excessive rate of capacity decay resembles that observed earlier (2017 Report) in poorly welded electrode mats. Properly welded electrode mats are getting ready for testing.
- Charge/discharge curves show increased voltage hysteresis with cycling, indicating increased cell impedance (presumably due to continual growth of the SEI layer as shown in previous SEM analysis).

OAK RIDGE National Laboratory

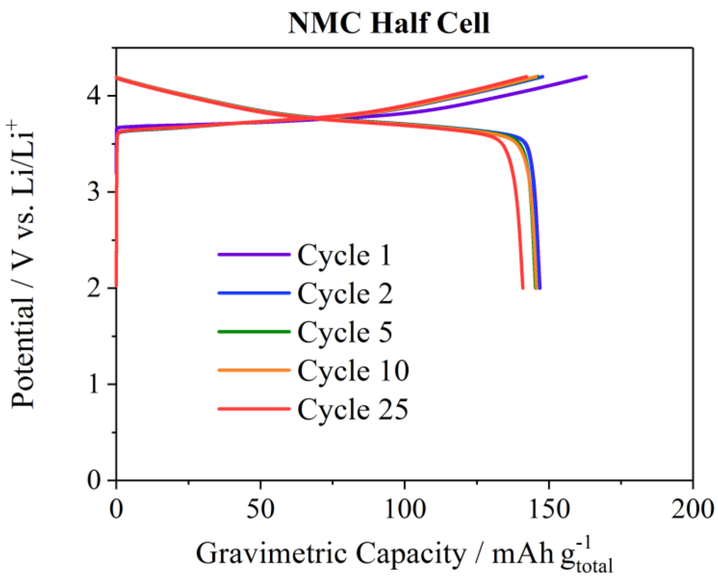
Technical Accomplishments and Progress

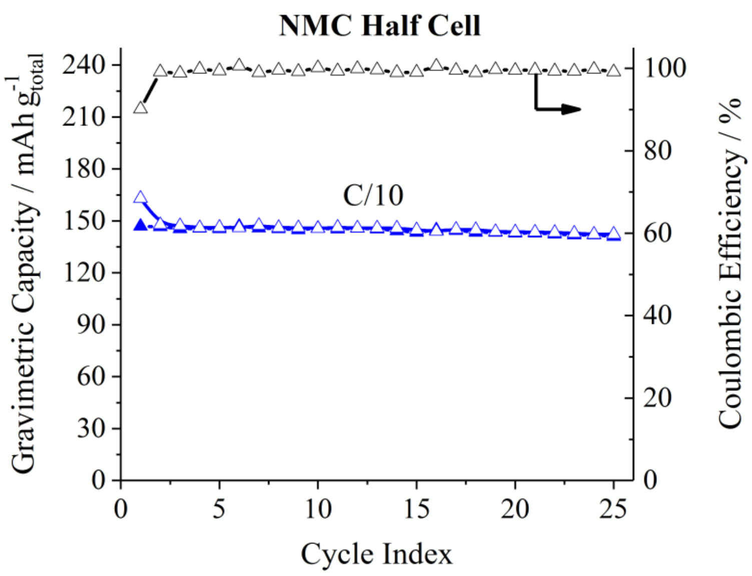
NMC622 Cathodes – Half Cell Studies (ORNL)

Cathode Composition (CAMP A-C018)
90 wt% NMC622 ($LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$)
5 wt% Conductive Carbon
5 wt% PVDF binder

Electrochemical Cycling Procedure
Li metal counter/reference electrode
Galvanostatic charge/discharge, 2.0 - 4.2 V
C/10 (25 cycles)

Electrolyte Composition
Gen 2 Electrolyte (1.2 M $LiPF_6$ in 3/7 EC/EMC)
+ 10 wt% FEC Additive





- NMC cathode exhibited an reversible capacity of 147 mAh/g_{total} (163 mAh/g_{NMC}) and good cycling stability (96% retention over 25 cycles).
- Negligible voltage hysteresis was observed with cycling.

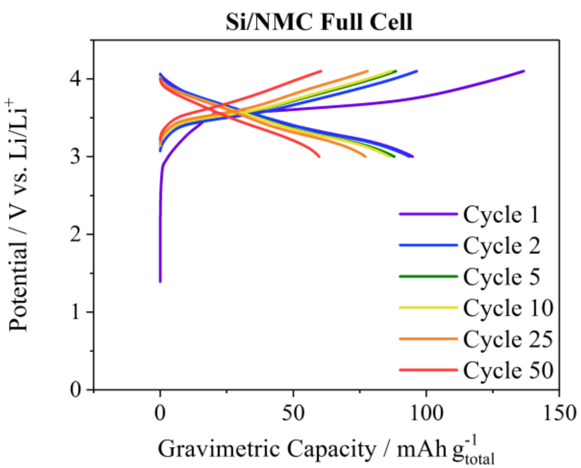
Technical Accomplishments and Progress

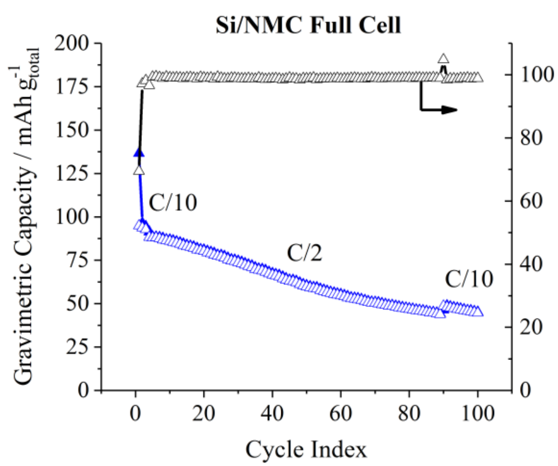
Full Cell Studies – Si Anode and NMC Cathode (ORNL)

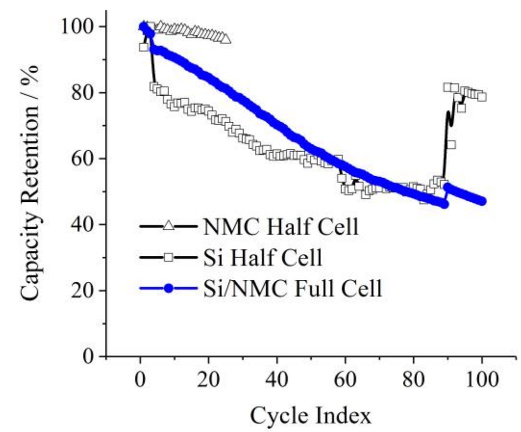
Cell Details
Dual Fiber Anode (DF 112917)
NMC622 Cathode (CAMP A-C018)
N/P Ratio ~ 0.84
$Q_{theoretical}$ ~ 127 mAh/gtotal (includes AM + C + binder for both electrodes)

Electrochemical Cycling Procedure
Galvanostatic charge/discharge, 3.0 - 4.1 V
C/10 (3 cycles), C/2 (86 cycles), C/10 (11 cycles)

Electrolyte Composition
Gen 2 Electrolyte (1.2 M $LiPF_6$ in 3/7 EC/EMC)+ 10 wt% FEC Additive







- Reversible capacity of 95 mAh/g_{total}
- Good Si utilization (3,300 mAh/g_{Si})
- Increased voltage hysteresis with cycling (consistent with Si half cell cycling results)

- Moderate capacity fade observed with cycling due presumably to insufficient fiber welding.
- Capacity fade rate of full cell closely matches that of Si half cell, indicating full cell performance limited by anode.
- Surprisingly, when current decreased from C/2 to C/10 (cycle 90), the full cell capacity did not recover, indicating Li inventory loss in the cell.

OAK RIDGE National Laboratory

Responses to Previous Year Reviewers' Comments

Comment by Reviewer 1*: A review of all work to-date should be conducted and then compared to work accomplished by other researchers.*

Response: Such a reviewing process is being conducted continuously and has been integrated into the work plan.

Comment by Reviewer 2*: The reviewer suggested that in addition to current work within the project, that scale-up approaches, such as roll to roll be considered.*

Response: Scale-up studies will be initiated the next year at eSpin Technologies, Inc.

Comment by Reviewer 3*: This reviewer observed that it seems difficult to build actual cells with any power capability, no current collector.*

Response: To address this comment, the project team has begun depositing (electrospinning) fibers directly onto a copper foil current collector.

Comment by Reviewer 4*: This reviewer warned that the testing results did not show cycle efficiency, which could be most important in order to see the improvement.*

Response: a summary of cycle efficiency data is shown on slide #14.

Collaboration and Coordination with Other Institutions

- **Lawrence Berkeley National Laboratory (Dr. Gao Liu):** Synthesize conductive polymer binders which are sent to Vanderbilt University for electrospinning (Year 1).

- **Oak Ridge National Laboratory (Dr. Jagjit Nanda and Dr. Ethan Self)**: Conduct electrochemical performance analysis of nanofiber anodes and provide microstructural and interfacial characterization of the electrospun materials.

- **e-Spin Technologies, Inc. (Dr. Jayesh Noshi):** Conduct preliminary scale-up of the electrospinning process at his commercial facility in year 3.

Remaining Challenges and Barriers

- Reducing content of the inert carriers/binders in the electrode (Reduction of the current level of inert polymers content 35-45wt.% could allow to increase the storage capacity).

- Increasing conductivity of the carbon fiber network, e.g., through addition of MWCNT, different carbons or metal (Sn?) particles (Reduction of the electrode electronic resistance would enable increasing the areal capacity and cycling efficiency).

- Improving compositional uniformity of the dual fiber electrodes (During the co-electrospinning the C/PAN and Si/PAA fibers repel each other and that sometimes leads to a nonuniform distribution, resulting in unacceptable variability of characteristics along the electrode). One possible solution would be the use of a static eliminator (ionizer).

Proposed Future Research

Budget Period 3 – Anode Optimization Studies and Scaling-Up Manufacturing

FY	Milestone	Type	Description
2018	Acceptable capacity and cycling stability demonstrated	Go/No-Go	Demonstrate a discharge capacity above 750 mAh/g, after 50 cycles at 0.1C and a capacity above 500 mAh/g after 50 cycles at 1C.
2018 2019	Best electrospun anode identified	Technical	Select the best conducting polymer binder for electrospinning with Si nanoparticles.
2019	Initial electrospinning at commercial facility successful	Technical	Demonstrate performance data for anodes.
2019	Electrospun anode scale-up successful	Technical	Demonstrate that the performance of scaled-up anodes matches/exceeds that from laboratory-fabricated anodes and meets the target performance metrics.

Any proposed future work is subject to change based on funding levels.

Summary

A new dual fiber anode mat morphology was created and successfully tested, for use in Li-ion batteries.

- Separate fibers were electrospun, for Li intercalation (Si/PAA fibers) and for electrical conduction (C/PAN fibers).
- Good charge/discharge behavior was observed up to 200+ cycles.
- Results show that there are sufficient contact points between Si/PAA fibers and C/PAN fibers in a dual fiber mat electrode for good isotropic electron flow throughout the anode, with good electrolyte infusion between fibers. 25% carbon fibers in a dual fiber mat is sufficient for acceptable electron conduction. However, the intrinsic conductivity of C/PAN fibers still needs to be increased.
- The inert polymer binder content in the electrode needs to be reduced and electrode compositional uniformity (the local uniformity in the number of Si and C fibers) needs to be improved.

Electrosprayed Si/C/PVAE-PAA anode mats can be a simplified alternative.

- New crosslinkable binders based on blends of poly(vinyl alcohol) (PVA) + PAA and poly(vinyl alcohol-co-ethylene) (PVAE) + PAA, were investigated. The PVA-PAA blend was shown to be thermally crosslinkable at 110^{o}C.
- Unfortunately, inks with these blends (containing both Si and C particles) could not be electrospun (at room temperature), so electrosprayed electrodes were fabricated and evaluated. Their performance was somewhat inferior to that of dual fiber electrospun electrodes.

To date, all project milestones have been met on schedule.